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THE AFTER-EFFECT OF HYDROSTATIC PRESSURE ON THE SILVER COLLOID IN SILVER CHLORIDE*

BY RYO KIYAMA AND KIYOSHI SHIMIZU

Introduction

The authors reported in the previous papers¹⁾ on the after-effect on the hydrostatic pressure on the color centers in alkali halides. Now, the authors have studied for the temperature effect and the after-effect of hydrostatic pressure on the Ag colloid produced photochemically in the AgCl crystal which is more ductile than alkali halide crystal and whose cation, Ag^+ , belongs to the same group as the alkali metal ion.

Experimentals

Preparation of single crystal and specimen For the preparation of the single crystal, first, the powder of AgCl was prepared as follows. The white turbidity of AgCl was produced in small degree by adding hydrochloric acid to aqueous ammoniac solution of 0.1 N silver nitrate and allowed to settle for the purpose of coprecipitating the impurities, which were contained in the starting material, with AgCl and then the precipitate was removed from the solution by filtration. It was found from the result** by means of the spectro-analysis that the impurities were removed from the solution by this coprecipitation method. Then, by adding the purified solution to excessive amount of 0.1N hydrochloric acid in vigorous stirring, the AgCl was precipitated. After the mother liquid was discarded by decantation, AgCl precipitate was digested with 0.1N hydrochloric acid, washed with voluminous water and dried at 130°C. From this AgCl powder, the single crystals were synthesized by S. Kyropoulos' method.

In order to obtain the specimens for this study, the plates of AgCl crystal, about 1.5mm thick, were sawn from the same single crystal block with the saw blade of tungsten-steel. The surfaces of the plate were so darkened by contact with the saw blade that the darkened parts were planed away with a glass edge and both surfaces were finished in almost parallel planes, and then the specimen, about $0.8 \times 13 \times 5$ mm, was prepared by rolling this plate with a glass rod, placing it between two pieces of flat glass plate and pressing. Hereafter, these specimens will be called the rolled

* This investigation has been done by K. Shimizu, being in the postgraduate course, under the direction of Prof. R. Kiyama.

** Unpublished.

1) S. Minomura, *This Journal*, 24, 28 (1954)

R. Kiyama, S. Minomura and M. Ōura, *Proc. Japan Acad.*, 30, 764 (1954)

R. Kiyama and K. Shimizu, *This Journal*, 25, 10 (1955)

specimens. The transmission* of these specimens in the infrared region ($1\sim 14\mu$), as shown in Fig. 1, was about 80% in the region of $2\sim 14\mu$. This value was in agreement

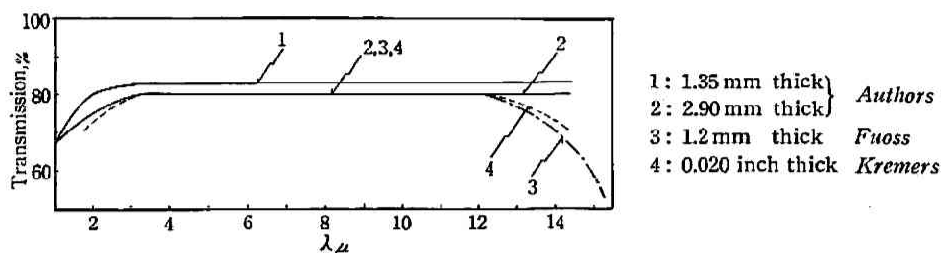


Fig. 1 Infrared transmission of silver chloride

with R. M. Fuoss' value²⁾ and H. C. Kremers' value³⁾ and was over the theoretical value (77%) which was calculated by Fuoss²⁾.

The annealing of the rolled specimens was performed at 200°C for 30 minutes and 5 hours, or at 400°C for 5 hours⁴⁾ and the specimens were cooled slowly to room temperature. These specimens will be called the annealed specimens.

The coloring of each specimen (rolled specimen and annealed specimen), was performed by irradiating both surfaces of each specimen for 30 minutes per one surface with the light of the carbon arc (diameter of carbon, 10mm; voltage, about 40 volts; current, 8~10 amp.) filtered through the cobalt glass placed in front of the specimen. The distance between the specimen and the carbon arc was 10cm. The temperature of the specimen increased with the lapse of irradiation time by the thermal radiation from the carbon arc and attained to the state of thermal equilibrium at 95°C in 30 minutes.

By the above method, when two pieces of the rolled specimen or annealed specimen were colored one by one, the concentrations of the color in the two pieces of specimen were not equal because of the fluctuation of the light source and the difference of the relative position of the specimen to the light source, but it was confirmed that the two pieces of the specimen, arranged near to each other and colored by irradiation at the same time, were colored equally, so that in the case that the standard specimen was needed for comparison, the specimens were colored by irradiation at the same time.

It was confirmed that this coloration was attributed to the Ag colloid produced in the specimen by irradiation with light.

Procedure In order to investigate the temperature effect and hydrostatic pressure effect on the Ag colloid produced photochemically in the rolled specimens and the annealed specimens, the experiments were performed as follows.

* The measurement of this part was performed by Mr. K. Inoue.

2) R. M. Fuoss, *Rev. Sci. Instr.*, **16**, 154 (1945)

3) H. C. Kremers, *J. Opt. Soc. Am.*, **37**, 337 (1947)

4) J. M. Hedges and J. W. Mitchell, *Phil. Mag.*, **44**, 357 (1953)

First, concerning the temperature effects, (1) the heating time effect and heating temperature effect on the rolled Ag colloid specimen were observed by means that the rolled specimens colored by irradiation with light were discolored by heating for a definite time (total 30 and 50 minutes) at a definite temperature (150~400°C) in an electric furnace and rapidly cooling in the air. (2) As for the annealing effect before coloring by irradiation with light, the annealed specimens that were prepared by annealing the rolled specimens at a definite temperature (200° and 400°C) for a definite time (30 minutes and 5 hours) were colored by irradiation with light and discolored by heating at 200°C for 30 minutes.

Concerning the pressure effect, (1) for the purpose of observing the effect of the hydrostatic pressure, which was applied to the specimen before coloring by irradiation with light, on the formation of Ag colloid by photolysis and the behavior of Ag colloid by heating, the noncolored rolled or annealed specimens were compressed in the mobil oil at 7,500kg/cm² for 24 hours by the ultra-high pressure apparatus⁵⁾ at room temperature. Whenever the specimens were compressed, they were protected from the direct contact with mobil oil by being wrapped in the envelope made of polyethylene. For the observation of the pressure effect on the formation of Ag colloid by photolysis, after compression, these rolled specimen and annealed specimens were colored with the corresponding atmospheric specimen for comparison by irradiation with light. Moreover, for the observation of the pressure effect on the behavior of Ag colloid by heating, these colored specimens were discolored by heating at 200°C for 30 minutes with the corresponding atmospheric specimens for comparison. (2) For the observation of the pressure effect on the rolled Ag colloid specimens, which had been discolored by heating after coloring by irradiation with light, the rolled specimens were colored by irradiation with light, discolored by heating at 200°C for 30 minutes and compressed at 1,000~7,500kg/cm² for ~65 hours.

The absorbance of the colored specimen, $\log_{10}(I_0/I)$ where I is the intensity of the transmitted light through the colored specimen and I_0 is the intensity of the transmitted light through the specimen before coloring by irradiation with light, was measured by means of Beckman model D U Quartz Spectrophotometer in the wavelength range from 420m μ to 1,000m μ and at the interval of 2m μ in the vicinity of the peak of the absorption band.

The preparation and the handling of the AgCl powder and its single crystal were performed under the photochemically inactive light.

Results

Effect of temperature

1) *Rolled specimen* In the rolled specimens, the absorption band having the flat peak (550~660m μ) was developed by irradiation with light (curve 1 in Figs. 2, 3

5) R. Kiyama and S. Minomura, *This Journal*, 22, 49 (1952)

and 4). This absorption band corresponded to that of Ag colloid produced photochemically in the AgCl crystal^{6,7)}.

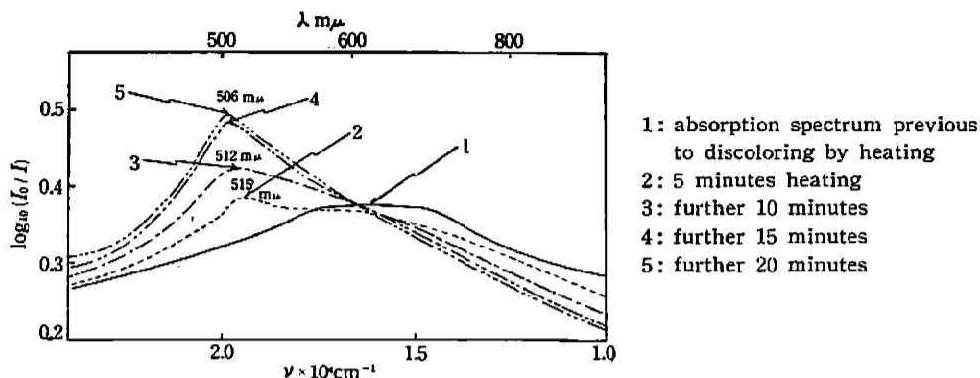


Fig. 2 Heating time effect on the absorption spectrum of the same rolled Ag colloid specimen (temp. of heating, 200°C)

The changes of the peak position of the absorption band and its height in this colored specimen with the lapse of the heating time (total 50 minutes) at 200°C or 300°C were as follows. In the case of heating at 200°C, as shown in Fig. 2, the peak position of the absorption band shifted to shorter wavelength side, 515 mμ ~ 512 mμ ~ 506 mμ and its height increased with the lapse of the heating time for 5 minutes, further 10 minutes and 15 minutes. After further 20 minutes heating, the peak height increased still more, but the change of the peak position could not be observed. In the case of 300°C, as shown in Fig. 3, the peak position shifted to the short wavelength side,

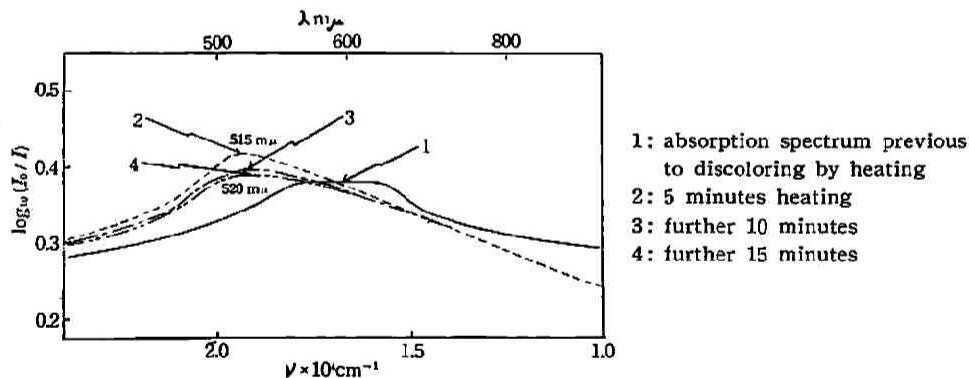


Fig. 3 Heating time effect on the absorption spectrum of the same rolled Ag colloid specimen (temp. of heating, 300°C)

515 mμ, and its height increased after 5 minutes heating, but after further 10 minutes heating, the peak position shifted to the long wavelength side, 520 mμ, and its height decreased. By further 15 minutes heating, the peak height was decreasing, but the decre-

6) R. Hilsh and R. W. Pohl, *Z. Physik*, **64**, 606 (1930); **77**, 421 (1932)

7) E. Rohloff, *ibid.*, **132**, 643 (1952)

ment of the peak height decreased with the lapse of the heating time, so that after further 20 minutes heating any change of the band could not be observed.

The changes of the absorption band of Ag colloid by heating at various temperatures, 150°C (the temperature of the specimen attained to 95°C by the thermal radiation from the carbon arc, so that the experiment was not performed at the temperature below 150°C), 200°, 300° and 400°C, for 30 minutes were shown in Fig. 4. The peak position

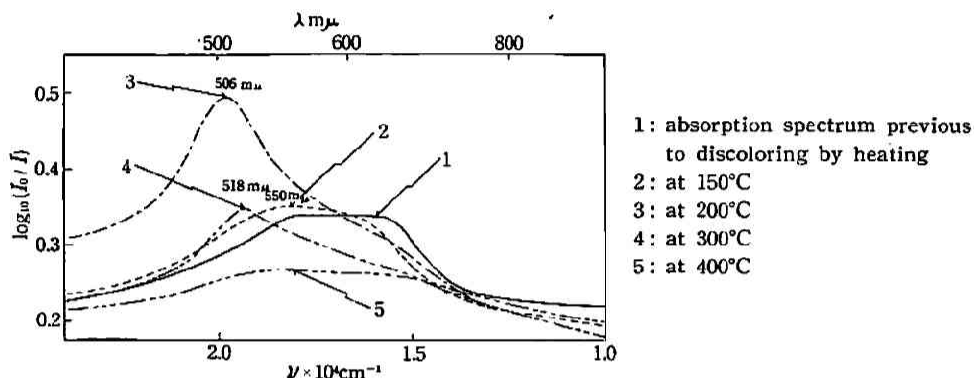


Fig. 4 Heating temperature effect on the absorption spectrum of the rolled Ag colloid specimen (time of heating, 30 minutes)

of the absorption band shifted to shorter wavelength side, 550 mμ (150°C), 506 mμ (200°C) and its height increased with increasing temperature of heating from 150°C to 200°C. But, at 300°C the peak position shifted to longer wavelength side, 518 mμ, from that at 200°C and its peak height decreased. At 400°C, the band height decreased much more and was lower than that in the initial state, and its shape became flat.

2) *Annealed specimen* The annealing effect was as follows; when the annealed specimens, which had been colored by irradiation with light, were discolored by heating at 200°C for 30 minutes, in the case of the specimen annealed at 200°C for 30 minutes, the peak position of the absorption band shifted to the short wavelength side, 506 mμ, as well as in the rolled specimen, but the increment of the peak height was not so large (Fig. 5). In the case of the specimen annealed at 200°C or 400°C for 5 hours, the peak position of the absorption band shifted to short wavelength side, 550 mμ (200°C)

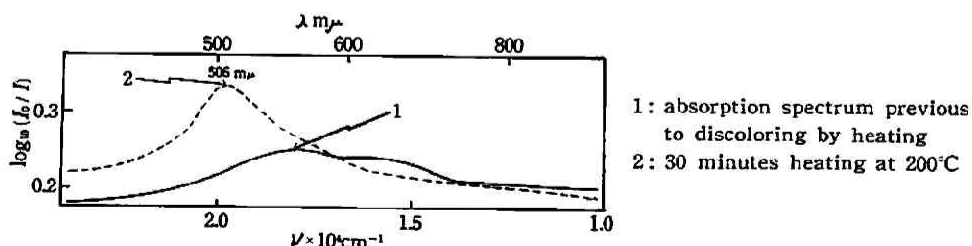


Fig. 5 Annealing effect on the absorption spectrum of the annealed Ag colloid specimen (temp. of annealing, 200°C; time of annealing, 30 minutes)

or $540\text{ m}\mu$ (400°C), but its peak height became lower than that in the initial state (Figs. 6 and 7).

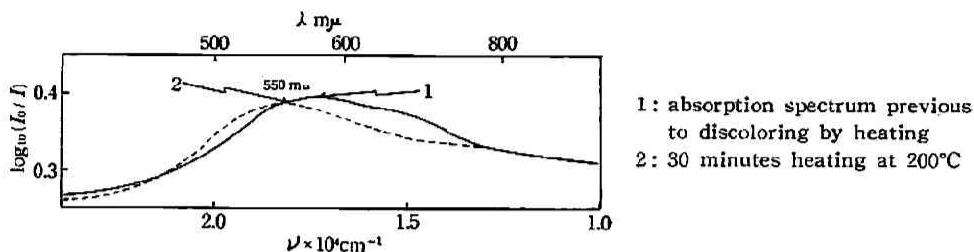


Fig. 6 Annealing effect on the absorption spectrum of the annealed Ag colloid specimen (temp. of annealing, 200°C ; time of annealing, 5 hours)

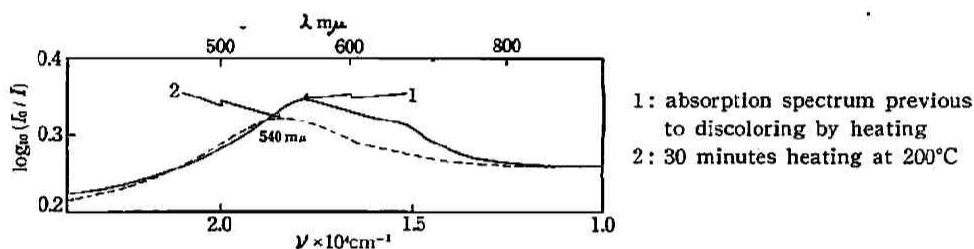


Fig. 7 Annealing effect on the absorption spectrum of the annealed Ag colloid specimen (temp. of annealing, 400°C ; time of annealing, 5 hours)

Effect of hydrostatic pressure

1) *Compression before coloring by irradiation with light* After compression at $7,500\text{ kg/cm}^2$ for 24 hours, the rolled specimen and the annealed specimens (200°C , 30 minutes; 400°C , 5 hours) were colored with the corresponding atmospheric specimen by irradiation with light at the same time, the absorption bands in these colored specimens were developed as shown by the curves 1 and 3 in Figs. 8, 9 and 10 respectively. In each figure, the peak height of the absorption band in the

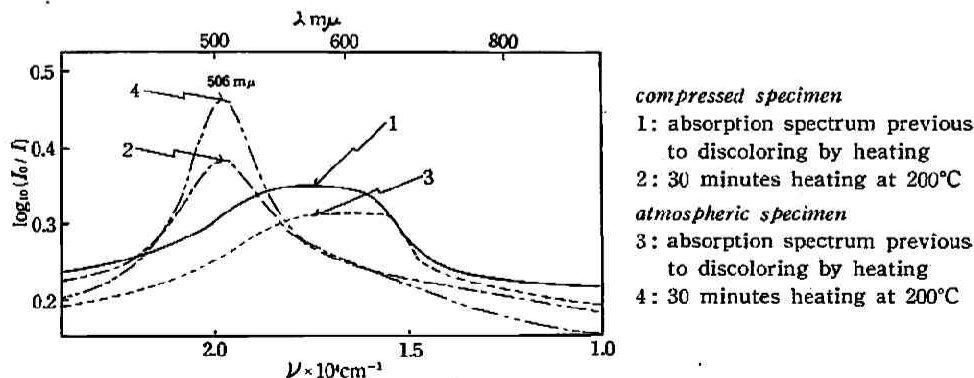


Fig. 8 Pressure effect on the absorption spectrum of the rolled Ag colloid specimen due to compression before coloring by irradiation with the light

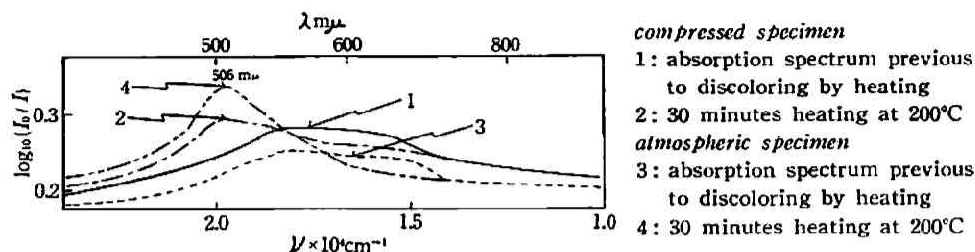


Fig. 9 Pressure effect on the absorption spectrum of the annealed Ag colloid specimen (temp. of annealing, 200°C; time of annealing, 30 minutes) due to compression before coloring by irradiation with light

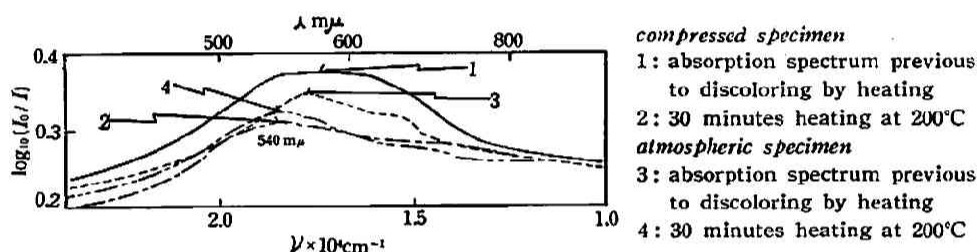


Fig. 10 Pressure effect on the absorption spectrum of the annealed Ag colloid specimen (temp. of annealing, 400°C; time of annealing, 5 hours) due to compression before coloring by irradiation with light

compressed specimen was higher than that in the corresponding atmospheric specimen. After discoloring by heating these colored specimens, as shown by the curves 2 and 4 in each figure, the peak positions of the absorption bands in the compressed specimens located at 506 $m\mu$ (rolled specimen and annealed specimen: 200°C, 30 minutes), 540 $m\mu$ (annealed specimen: 400°C, 5 hours) as same as in the corresponding atmospheric specimen, but the increment of the peak height of the absorption band in the compressed specimen by discoloring was smaller than that in the corresponding atmospheric specimen.

2) *Compression after discoloring by heating* The after-effect of the hydrostatic pressure on the rolled specimen discolored by heating at 200°C for 30 minutes after coloring by irradiation with light, was as follows. After compression at 1,000 kg/cm^2 for 1 hour any change of the absorption band could not be observed. At 3,000 kg/cm^2 for 1 hour, the absorbance decreased a little and the broadening of the peak was observed. The decrease of the absorbance by compression was larger with increasing pressure from 5,000 kg/cm^2 to 7,500 kg/cm^2 for 1 hour and flat peak (500~510 $m\mu$) was observed (curves 2 and 3 in Fig. 11). After compression for 24 hours at 7,500 kg/cm^2 , the decrement of the absorbance became larger than in the case of compression for

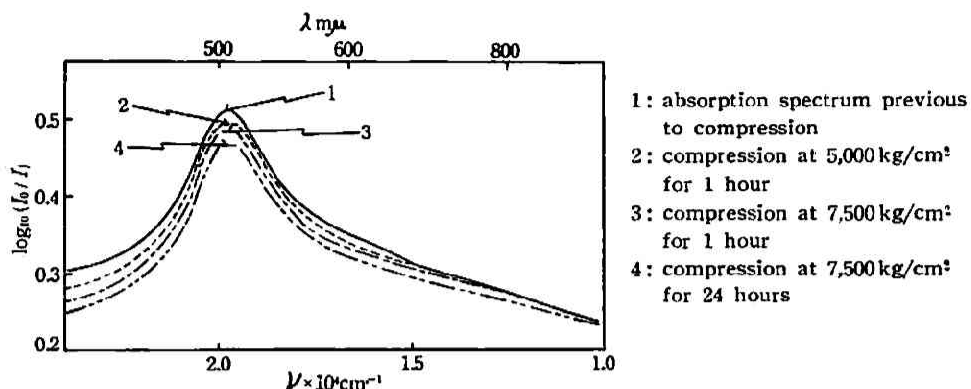


Fig. 11 Pressure effect on the absorption spectrum of the rolled Ag colloid specimen due to compression after discoloring by heating

1 hour at 7,500 kg/cm² (curve 4), but the decrement of the absorbance by compression for longer time did not differ from that in the case of the compression for 24 hours.

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